

The kinetics of nucleation and growth from grain boundaries: a mean field approach

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Abstract

A model for phase transitions initiated at nucleation sites on grain boundaries is proposed and tested against numerical simulations: a mean field approach allows to explicitly consider the granular structure, yielding accurate predictions for a wide span of nucleation processes. Comparisons are made with classical models of homogeneous as well as heterogeneous nucleation. While it is shown that the standard theory of homogeneous nucleation fails at predicting the nucleation kinetics from the interfaces, it is additionally shown that the accuracy of the usual model of heterogeneous nucleation diminishes as the nucleation rate increases, while that of the presented model is enhanced.

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Recrystallization is a mechanism of great scientific and technological importance, encountered during the thermomechanical processing of various materials including metals [1]. The first model that efficiently captures the main features of recrystallization, namely the JMAK model, states that grains nucleate from points of random locations, and that the grains grow at a constant velocity, until impinging other neighboring growing grains. Thanks to its straightforwardness, this model was also used in many other situations, provided that the hypotheses of random nuclei and independent growing zone are met: combustion [2], particle physics [3], evolution of damage under dynamic tensile loadings, to mention only a few, making the JMAK model a much encountered approach.

Random distribution of nuclei is however a rather crude hypothesis. To give examples, materials experience damage by crack nucleation preferably at grain boundaries [4, 5], combustion of solid energetic materials starts at preferred sites [6], nucleation of grains during recrystallization appears at prior grains frontier [7], and crystallization can be influenced by confinement in a porous media [8] or contact with grain boundaries of an other material [9]. Thus, the problem of nucleation from interfaces is encountered in a variety of fields [10–14] and the importance of structured nucleation sites - inner nucleation free volumes bounded by interfaces - as well as grain size dependence is commonly witnessed [15, 16].

In this regard, extensions of the JMAK model have been proposed over the years to take into account the specificities of structured nucleation. Most derivations still consider random distribution of nuclei, improving only marginally the model, by fitting a so-called JMAK parameter [17] with no clear physical justification [18–21].

One of the major improvement of the JMAK model that faces the problem of nucleation heterogeneity has been proposed by J.W. Cahn and considers nuclei distributed on planar interfaces [15, 22]. This approximation extends the predictions to nucleation at grain boundaries, provided that the density of nucleation sites remains low enough. Cahn’s main assumption is that the superimposing planes are randomly located, whereas an accurate modeling for the higher nucleation densities requires to capture the deterministic nature of the location of nucleation -the grains boundaries-, excluding grain volume as a possible nuclei source. In other words, an assembly of random planes is a coarse description of interfaces in a granular material.

In this Letter, we propose an accurate modeling of the kinetics of grain nucleation and growth that takes explicitly into account grain boundaries as preferred sites for nuclei. A

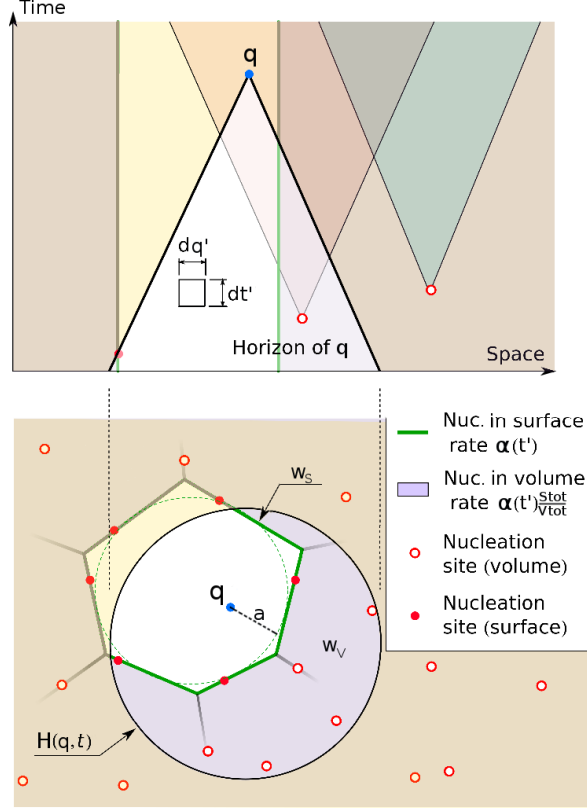


FIG. 1: Upper picture: Schematic representation of the horizon of a point q in a time-space diagram. Nucleation points are represented as red dots, with their associated (shaded) cone of transformation. The grain is represented by the two green lines. Lower picture: Schematic representation of the two sets of nucleation sites within a slice of $H(q, t)$ at a given nucleation time t' , on interfaces (closed red dots) with intensity $\alpha_S(t') = \alpha(t')$ and in volume (open dots) with intensity $\alpha_V(t') = \frac{S_{tot}}{V_{tot}} \alpha(t')$. Point q can be transformed only by a nucleation inside its horizon $H(q, t)$.

characteristic length L_n is introduced and compared to the average grain size L_g , allowing for a detailed analysis of the interplay between length scales of initial microstructure and reacted one. It is shown that for high nucleation rates, the reacted volume is dictated by the granular structure only, leading to a deterministic behavior of the nucleation process. On the other hand, for a decreasing site density, the effect of microstructure progressively vanishes whereas the probabilistic nature of the nucleation process increases. The validity of this modeling is supported by simulations of reactions (phase transition, combustion, damage, ...) initiated by random nucleation on the interfaces of a Voronoi tessellation.

Once nucleated at time t' , a transformation zone expands from the nucleation site over a

maximum travel distance given by $h_{t'}(t) = \int_{t'}^t c(s)ds$, $c(s)$ being the expansion celerity and t the present time. All potential nucleation sites in this expansion zone then become inhibited. Thus, a nucleation point q' is inhibiting all nucleation in a time-growing transformed zone of radius $h_{t'}(t)$.

Considering a random point q , a nucleation event taking place at time t' at a distance from it smaller than $h_{t'}(t)$ is close enough to be certain to transform q before or at time t . Therefore the probability P_{\exists} that q is transformed at time t by a nucleation that previously occurred is given by the probability of at least one nucleation occurring in its horizon $H(q, t) = \{(x, t'), \|x - q\| \leq h_{t'}(t)\}$ consisting in the time-space that can influence the considered point q . The probability of at least one event P_{\exists} is complementary to the probability of no nucleation event occurring $P_{\bar{\exists}}$ and will be determined this way. As P_{\exists} is expressed for any point, this probability is identified as the ratio of transformed volume at time t , $\Phi(t) = \frac{V_{trans}(t)}{V_{tot}} = P_{\exists}(t)$. A schematic representation of the time horizon in a time-space diagram is proposed in the upper picture of Fig. 1.

Considering an untransformed element q_i of volume Δq over a short time interval Δt beginning at t_j , and taking them small enough so that the nucleation rate α can be considered as constant, then nucleation will occur in this element (q_i, t_j) with a probability given by:

$$P(q_i, t_j) = \alpha(q_i, t_j) \Delta q \Delta t \quad (1)$$

The probability that no nucleation occurs in a horizon $H(q, t)$ can be calculated as a product of probabilities over the horizon itself:

$$P_{\bar{\exists}}(q, t) = \prod_{(q_i, t_j) \in H(q, t)} (1 - \alpha(q_i, t_j) \Delta q \Delta t) \quad (2)$$

This expression leads to the following equation when Δq and Δt are infinitely small:

$$\begin{aligned} \Phi(t) &= 1 - P_{\bar{\exists}}(q, t) = 1 - \exp \left(- \int_{H(q, t)} \alpha(q', t') dt' dq' \right) \\ &= 1 - \exp(-N(q, t)) \end{aligned} \quad (3)$$

with $N(q, t)$ built as the average number of nucleation events over the horizon $H(q, t)$. In case of a transformation propagating at constant celerity c , the horizon is a set of spheres of radii $h_{t'}(t) = c(t - t')$. If the nucleation is assumed to be homogeneous (spatially random)

and time independent, then the nucleation rate can be extracted out of the integral, and the JMAK model for homogeneous nucleation is immediately recovered, integrating over t' , and yields for a 3D system:

$$\Phi(t) = 1 - \exp\left(-\frac{\pi}{3}\alpha c^3 t^4\right) \quad (4)$$

For the more general case of granular materials, the nucleation rate is known to depend on the local structure, and exhibit different values for nucleation occurring in the bulk or at the grain boundaries [22]. The following development aims at predicting the contribution of grain boundary nucleated phase transformation only.

Our model is grounded on a simplified representation of an assembly of grains, composed of spherical grains surrounded by a homogeneous material. Inside of those spherical grain the probability of transformation is thus isotropic and depends only on the distance from the grain boundary. Considering a particular grain, nucleation can occur on its surface (with intensity $\alpha(t)$) or beyond with an intensity approximated by the average nucleation rate over the whole volume, $\alpha(t)\frac{S_{tot}}{V_{tot}}$, as depicted in the lower picture of Fig. 1.

We will now express the fraction of transformed volume $\Phi(t)$, which now depends on spatial coordinates due to the inhomogeneity of the nucleation. Let us consider a certain grain of radius r and inside of it, a certain point q_a at a distance a from the grain boundary. From there we can express the average number of nucleation events $N(q_a, t) \equiv N_r(a, t)$, over the horizon $H(q_a, t)$, simply as a function of the distance a of q_a from the nearest grain boundary and of the grain's radius r .

By noting that nucleation is not possible inside of a grain, the volume integral in equation 3 can be split into two terms, accounting for nucleation at the surface of the current grain of radius r , noted S_r and from the rest of the material, noted $\overline{V_r}$. The first term reduces to an integral over a surface defined by the intersection of the horizon with the current grain boundaries, and the second term corresponds to the average contribution of all other grain surfaces:

$$N_r(a, t) = \int_{S_r \cap H(q_a, t)} \alpha(t') dq' dt' + \frac{S_{tot}}{V_{tot}} \int_{\overline{V_r} \cap H(q_a, t)} \alpha(t') dq' dt' \quad (5)$$

In order to calculate $S_r \cap H(q_a, t)$ and $\overline{V_r} \cap H(q_a, t)$, we define w_S , the fraction of current grain's surface S_r intersecting the horizon, which is a function of grain radius r , of the distance a from the grain boundary, and of the propagation time $\tau = t - t'$ between a past

event occurring at t' and the current time t :

$$w_S(r, a, \tau) = \begin{cases} 0 & \text{if } c\tau < a, \\ \pi [c^2\tau^2 - a^2] \left(\frac{r}{r-a}\right) & \text{if } a \leq c\tau \leq 2r - a, \\ 4\pi r^2 & \text{if } c\tau > 2r - a \end{cases} \quad (6)$$

and w_V the fraction of the volume $\overline{V_r}$ intersecting the horizon:

$$w_V(r, a, \tau) = \begin{cases} 0 & \text{if } b < 0, \\ \frac{4}{3}\pi c^3\tau^3 - \frac{\pi}{3}(c\tau + a - b)^2(2c\tau - a + b) & \\ -\frac{\pi}{3}b^2(3r - b) & \text{if } 0 \leq b \leq 2r, \\ \frac{4}{3}\pi c^3\tau^3 - \frac{4}{3}\pi r^3 & \text{if } b > 2r \end{cases} \quad (7)$$

with $b = \frac{c^2\tau^2 - a^2}{2(r-a)}$. For a given grain radius, the investigated integral $N_r(a, t)$ is now expressed as a simple time convolution:

$$N_r(a, t) = \int_0^t \left[w_S(r, a, t - t') + w_V(r, a, t - t') \frac{S_{tot}}{V_{tot}} \right] \alpha(t') dt' \quad (8)$$

The points inside of the grain and located at a distance a from the grain's boundaries define a surface of constant probability of transformation $[1 - \exp(-N_r(a, t))]$, corresponding to the transformed fraction of this surface. As the probability of transformation of a point in a grain depends solely on its distance from the grain boundary a , we can now express the transformed fraction of a grain $\Phi_g(t, r)$ as an integration towards its center following a homothetic path:

$$\Phi_g(t, r) = \frac{3}{r} \int_0^r [1 - \exp(-N_r(a, t))] \left(\frac{r-a}{r}\right)^2 da \quad (9)$$

Thus we determined the transformed fraction of a grain $\Phi_g(t, r)$ given its radius r and are now able to express the global transformed fraction $\Phi(t)$ as an integration over the grain size distribution $f(r)$.

$$\Phi(t) = \int_0^\infty \Phi_g(t, r) f(r) dr \quad (10)$$

However approximated, the presented model is exact for two important limit cases. For very low nucleation rates $\alpha(t)$, the transformation of a point is most likely to be caused by a nucleation outside of the current grain, and N becomes significant only for time $ct \gg r$, when $w_S = 4\pi r^2 \ll w_V = \frac{4\pi}{3}[(t - t')c]^3$. The transformed fraction $\Phi(t)$ then reduces to

$\Phi(t) = 1 - \exp(-N)$ with $N = \frac{4\pi}{3} \int_0^t \alpha(t') [c(t-t')]^3 dt'$, the classical solution of the JMAK model.

Contrarily, a nucleation rate high enough ensures that $[1 - \exp(-N)] = 1$ for $a \leq ct$ (and 0 otherwise), yielding the exact expression of the homothetic transformations of an assembly of regularly shaped grains once injected in Eq.9: $\Phi(t) = \frac{3}{r} \int_0^{\min(ct, r)} \frac{da}{((r-a)/r)^2} = [1 - [(r - \min(ct, r))/r]^3]$.

This model allows for a continuous representation of nucleation from heterogeneous to homogeneous cases. If the grain boundaries are saturated with nucleation events the microstructure of the system dictates the kinetics of the transformation. On the contrary, if the nucleation events are rare enough they are not spatially correlated and appear to be randomly distributed. We will now examine the condition of transition between these two extreme behaviors.

We propose to define a characteristic time t_c as the time required for one nucleation event to happen on average in a characteristic zone which extent is given by $Z(t) = kc^n t^n$ for dimension n ($n = 2$ for site saturated nucleation, $n = 3$ for diffuse nucleation), with k a shape parameter ($k = \pi$ in 2D and $k = \frac{4\pi}{3}$ in 3D). The previous condition of one nucleation event on average, for a constant nucleation rate:

$$\int_0^{t_c} \alpha_n k c^n (t_c - t')^n dt' = 1 \quad (11)$$

leads to the characteristic time:

$$t_c = \left[\frac{n+1}{\alpha_n k c^n} \right]^{\frac{1}{n+1}} \quad (12)$$

with $\alpha_2 = \alpha$ and $\alpha_3 = \alpha S_{tot}/V_{tot}$ (nucleation on surface averaged over the volume). The radius of the characteristic zone at t_c defines a characteristic length L_n , function of space dimension n , representing the average distance between nucleation sites:

$$L_n = \left[\frac{c(n+1)}{k\alpha_n} \right]^{\frac{1}{n+1}} \quad (13)$$

For $n = 2$, L_2 should be orders of magnitude smaller than the grain size L_g to guarantee the 2D nucleation hypothesis. In the other hand, for $n = 3$, homogeneous nucleation can only hold when L_3 is compatible with an averaging over numerous grains, that is for $L_3 \gg L_g$. A possible transition definition is to consider the frontier between the two domains, at $L_2 = L_3$ leading to a definition of a transition scale $L_{trans} = \left(\frac{V_{tot}}{S_{tot}} \right)$.

Nucleation can thus be defined as homogeneous or heterogeneous depending on how the characteristic length L_n compares to this transition scale. If L_n is smaller than L_{trans} , the characteristic zone containing one nucleation site is fixed by the granular structure and the heterogeneity of the system is of importance to its dynamics. On the contrary, if L_n is of the same order of magnitude as L_{trans} , the characteristic zone containing one nucleation point is not imposed by the granular structure and the system can be considered as homogeneous. This transition is observed on Fig. 2, where the error between simulations results and different models are plotted over the ratio L_3/L_2 , showing that the presented model yields accurate predictions over the entire domain.

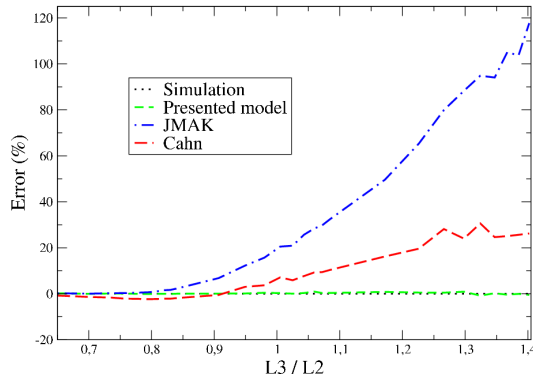


FIG. 2: Simulations of three-dimensional transformations nucleated from the interfaces (Voronoi tessellation) of a granular structure. Error of the models at the time at which the JMAK model predicts a complete transformation. The Mathematica program computing the presented model is supplied as online supplemental material.

Two applications of the presented model are proposed: the kinetics of recrystallization of a steel, and the kinetics of crystallization of a copolymer. The relevant physical parameters are obtained or estimated from published results [23–25]: the grain size distribution f and nucleation rate α are derived from the analysis of the materials' microstructure, and the celerity of the transformation is estimated as $R_g/t_{100\%}$ with R_g the average grain radius and $t_{100\%}$ the time for complete transformation. The results on Fig. 3 show that the JMAK model is completely unable to capture the kinetics of heterogeneous nucleation and growth of a transformation (unless fitted without physical justification). It also shows that Cahn's extension of JMAK can be very accurate in some systems (here the recrystallization of

steel) provided its microstructure is close to random planes. Additionally it shows that after inputting physical parameters, the presented model can reproduce with accuracy the kinetics of a transformation, demonstrating the importance of the microstructure's geometry as regards transformation initiated by heterogeneous nucleation.

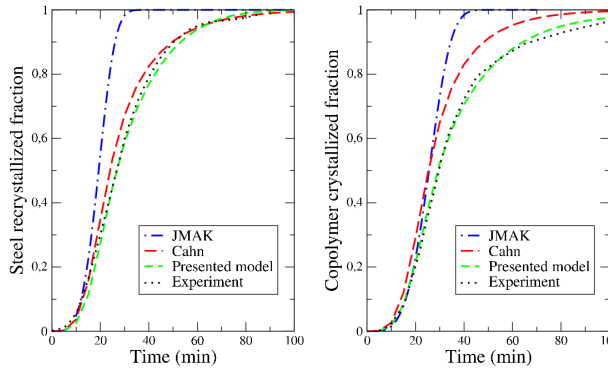


FIG. 3: Experiments against models. Left: Recrystallization of an interstitial-free steel at 630°C (70% cold rolled IF steel in [23]). Right: Crystallization of a propylene-ethylene copolymer at 110°C (PE 5.8 in [24, 25]).

We believe that the presented model has even more general applications as the mean field approach coupled with the space-time horizon method allows the modeling of the kinetics of any complex structure, Eq. 8 considering its sub-domains separately. Notably, the elongated form of very anisotropic grains such as those encountered in certain varieties of steel can be taken into account explicitly through a modification of expressions 6 and 7. Additionally, the kinetics of more complex nucleation processes can easily be retrieved such as a nucleation rate depending on temperature, through the modification of α ; or type of grain, through the modification of α and the use of a grain distribution f considering grain variety; or a different rate for bulk or surface nucleation, through the addition of a bulk term with a bulk nucleation rate in Eq. 8.

In conclusion, we have proposed a model for the kinetic of phase transformation nucleated at interfaces. We showed that the use of a mean field approach allows to reconcile heterogeneous and homogeneous nucleation in a single model, and that hypotheses on the regularity of the granular structure make it possible to solve our problem with great accuracy even for very irregular structures such as Voronoi tessellations.

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